

ENTHALPIES OF FORMATION OF CYCLIC CIS AZO N-OXIDES. ON THE QUESTION
OF VICINAL IN-PLANE LONE-PAIR REPULSION.¹

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Abstract

Previous workers have proposed that *cis* diazenes are less stable than the *trans* isomers as a result of nitrogen-nitrogen lone-pair repulsion. Based on thermochemical measurements, the inherent instability of the *cis* moiety has been placed at 33-34 kJ mol⁻¹ by Engel.

The lone-pair lone-pair repulsion hypothesis has been tested in the present work by examining the change in strain energy of a series of diazene N-oxides, substances in which one of the nitrogen lone electron pairs has been replaced by an N-O bond. Enthalpies of formation for five cyclic/polycyclic diazene N-oxides, the first known, have been measured to this end. Subsequent comparison of the resulting strain energies of the N-oxides with those of three corresponding diazenes, all relative an Allen bond energy scheme, indicates no variation either qualitatively or quantitatively.

A model for electron-pair electron-pair repulsion is proposed based on two electron Coulomb repulsion integrals over localized molecular orbitals (LMO) within the PRDDO framework. The analysis concludes that all types of sigma bond repulsions - *lp-lp*, *lp-bond* and bond-bond - are of comparable magnitude. However, the sum of the C-H/C-H repulsions dominate the calculated interactions by many-fold. It is further concluded that for acyclic diazenes and their N-oxides, classic steric repulsion effects (e.g. methyl-methyl) are largely responsible for the observed configurational energy relationships.

Introduction

Putative lone-pair lone-pair interaction has fascinated chemists as a source of the conformational preference observed in molecules containing hetero-atoms linked, geminal and vicinal to one another. For saturated or sigma-bonded systems, designations such as "gauche",³ the "anomeric"⁴ and the "rabbit-ears"⁵ effect are now commonplace. Substantiation of the importance of non-bonded electron-pair interaction has been forthcoming from photoelectron spectroscopy⁶ (PES) and quantum mechanical calculations.⁷ Although alternative viewpoints have been expressed,⁸ the lone-pair lone-pair concept endures.

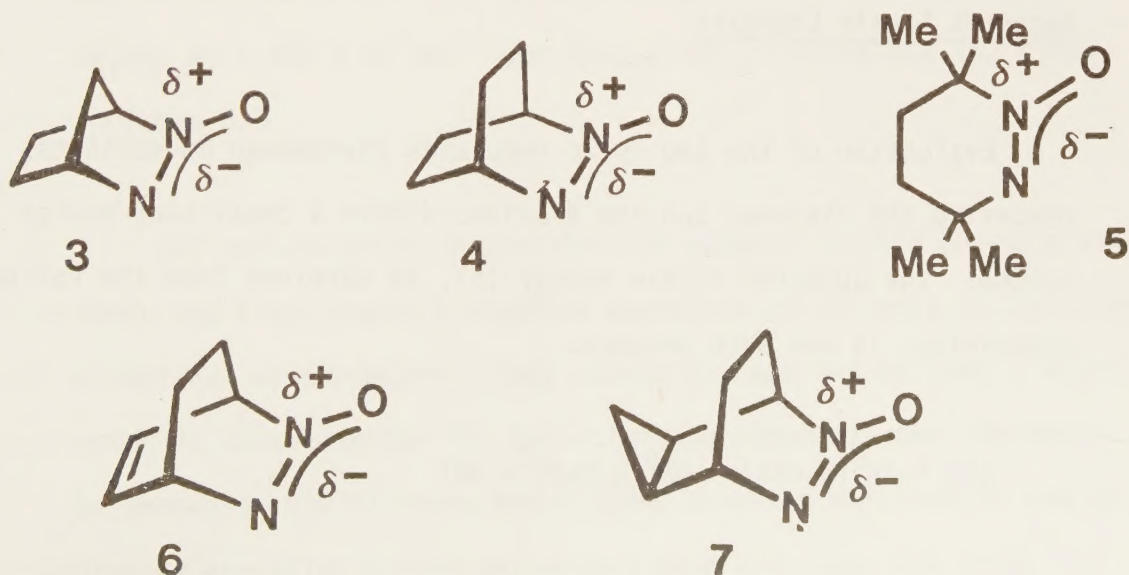
An interesting application of these ideas to a geometrically more constrained system involves the disposition of the nitrogen lone-pairs in the planar *cis* (1) and *trans* (2) azoalkane moieties. Here, too, UV,⁹ photoelectron spectroscopy¹⁰ and MO calculations^{10, 11} are unambiguous in their description that the nitrogen nonbonding electrons interact strongly and repulsively.

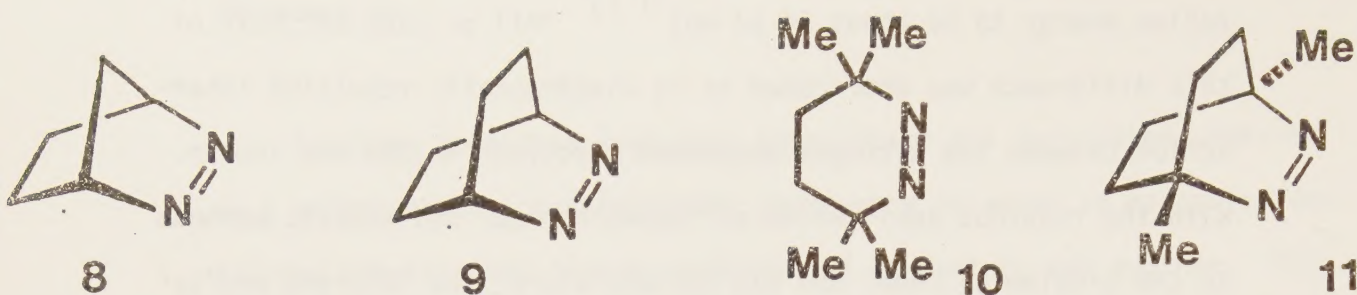


Long before the serious application of PES and MO methods to an exploration of the electronic structure of azo compounds, it was known that the *cis* azo configuration is thermodynamically less stable than the *trans* geometry.¹² In the case of di-*t*-butyldiazene (*t*-Bu-N=N-*t*-Bu), Mill and Stringham estimated the *cis-trans* isomeri-

zation energy to be about 84 kJ mol^{-1} .¹³ "All or part of" half of this difference was attributed to an electrostatic repulsive interaction between the nitrogen nonbonded electrons in the *cis* isomer. With the rigorous application of thermochemical and kinetic methods to the problem by Engel and his collaborators, the inherent energy gap separating the *cis* and *trans* diazene geometries has been suggested to be 33.5 kJ mol^{-1} favoring the latter.^{14, 15} Again mutual nitrogen lone-pair (*lp*) repulsion, ameliorated by variations in the N-N-C angle, was suggested as the origin of the energy difference.^{14, 15}

A means of testing the *lp* repulsion hypothesis is to be found in the replacement of one of the lone pairs by a bond, followed by subsequent evaluation of the energetic consequences of the resulting *cis/trans* isomeric pair. Accordingly, we have measured the gas phase enthalpies of formation for five polycyclic *cis* diazene N-oxides 3-7, the first known ΔH_f^0 's for the cyclic derivatives. Apparent strain energies have been calculated and compared with the corresponding quantities for the three iso-structural azoalkanes 8-10. The strain values are then interpreted in terms of an MO analysis based on electron repulsion between localized molecular orbitals.





Calorimetric Measurements

Combustion calorimetry as described in the experimental section was performed for N-oxides 3-7. A summary of the results is given in Tables 1 and 2. The Δu_C^0 values refer to the idealized reaction in which all reactants and products are in their thermodynamic standard states at 298.15 K. Sublimation enthalpies determined by vaporization calorimetry are listed in Table 3. Combination of the intermediate results provides standard molar energies, ΔU_C^0 , and enthalpies of combustion, ΔH_C^0 , and derived enthalpies of formation, ΔH_f^0 , for the solid and the gaseous states of the five azoxy compounds at 298.15 K (Table 4).

Apparent Strain Energies

Evaluation of the azo $lp-lp$ repulsion phenomenon necessitates comparing the diazenes and the N-oxides within a consistent energy scheme. The apparent strain energy [S], as obtained from the following expression, is one such measure.

$$[S] = \Delta H_f^0(g, \text{obs}) - \Delta H_f^0(g, \text{ref}) - mRT$$

The reference compounds are hypothetical strain-free isomers.

The enthalpies of formation of the gas phase reference compounds have been calculated by means of the Allen bond energy scheme.¹⁶ The quantity *m* refers to the number of rings in the molecule.¹⁷ Recently, the enthalpies of formation of some open-chain diazenes and diazene N-oxides were employed together with Allen parameters from Ref. 16 to derive $\Delta H_f^0(g)$ parameters specific for the -N=N- and -N=N(O) moieties.¹⁸ We have utilized these / parameters to calculate [S] values for the N-oxides 3-7. They are listed together with the same quantity for three of the corresponding diazenes (8-10) in Table 5.

The enthalpy of formation of diazene 9 has been estimated from the corresponding azoalkane with methyl groups bonded to the bridgehead carbons, 11. The difference in $\Delta H_f^0(g)$ between these two compounds in terms of Allen scheme parameters is:

$$\begin{aligned} \Delta(\Delta H_f^0(g), \underline{9-11})) &= -2B(C-C) - 4B(C-H) - 2\Delta_{CCC} - 4\Gamma_{CCC} - 2\Gamma_{CCN} \\ &\quad - 4\Delta_{CCN} = 71.2 \text{ kJ mol}^{-1} \end{aligned}$$

This is to be compared with 73.5 and 78.0 kJ mol⁻¹ derived from two different force field calculations.^{19, 20} The resulting $\Delta H_f^0(g, \underline{9}) = 163.6 \text{ kJ mol}^{-1}$ was thus used to obtain the [S] cited in Table 5.

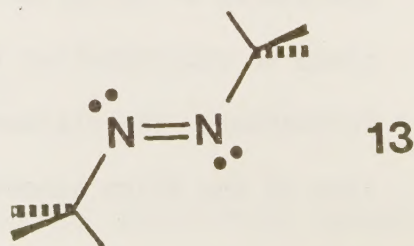
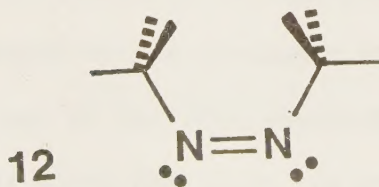
The uncertainties quoted for the apparent strain energies are twice the final overall standard deviation of the mean of the observed enthalpies of formation. They should be regarded as lower limits, since no uncertainties for the reference compounds are included. Furthermore, the diazenes and diazene N-oxides utilized in the derivation of the Allen scheme parameters were all *trans* and hence the

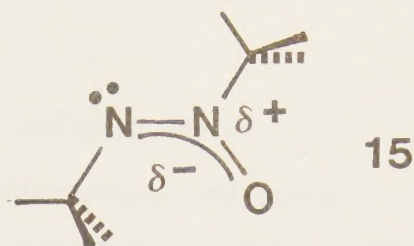
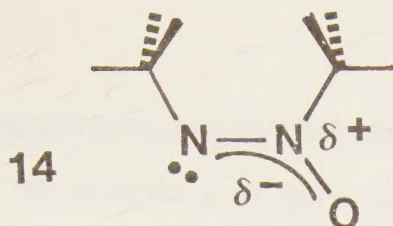
[S] values refer to hypothetical *trans* isomers. Thus the apparent strain energies contain a contribution from the energy of *trans* to *cis* isomerization for the -N=N- and -N=N(O)- groups, respectively.

Analysis of the Strain Energies

The question to be addressed in this section concerns the relative strain energy of a given azoalkane versus its N-oxidized counterpart. That is, does replacement of one of the diazene nitrogen *lp*'s with an N-O bond alter the overall molecular strain or leave it unchanged? Since it has been assumed that the acyclic compounds studied (with the exception of di-*t*-butyldiazene N-oxide) are strain-free,^{14, 18, 19} the answer can be found only by examining the cyclic series.

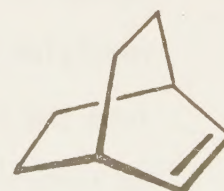
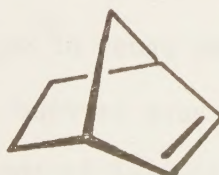
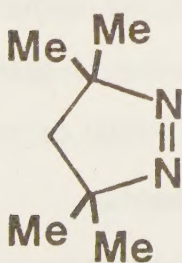
It is evident from the [S] values of Table 5 that the *cis* N-oxides are found to be 2.2-13.3 kJ mol⁻¹ more strained than the corresponding *cis* azoalkanes. To place this in context, it must be remembered that the calculated strain energies include an implicit component from the *cis*→*trans* isomerization energies. As these quantities are, to our knowledge, not available for a comparable pair of -N=N-/-N=N(O)- structures, we have made an effort to estimate them by quantum mechanical methods. The geometries of *cis* and *trans* azomethane (12 and 13) were taken from the literature. Those for azoxymethane (14 and 15) were fully geometry optimized with both PRDDO²¹ and the 4-31G split valence basis set.²² The results are cited in Table 6.





At the PRDDO level, the *cis* diazene configuration is less stable than the *trans* by 27.6 kJ mol^{-1} , while the difference is 41.5 kJ mol^{-1} for the N-oxide isomers. Thus, PRDDO suggests that the *cis*→*trans* isomerization energy for the latter is 13.9 kJ mol^{-1} greater than for the former. The 4-31G calculations yield a difference of 17.6 kJ mol^{-1} . If these values or their average is used to correct for the implicit *cis*→*trans* interconversion energy, the $\Delta[S](\text{azo-azoxy})$ gaps are reduced to 13.6 , 5.3 and 2.5 kJ mol^{-1} for pairs 8/3, 9/4 and 10/5 respectively. From this viewpoint, the azo-norbornene 8 represents a maximum strain of 13.6 kJ mol^{-1} over the analogous N-oxide. Thus, in the three cyclic cases evaluated here, the strain energies of the *cis* -N=N-/-N=N(O)- pairs are the same within the combined errors from experiments and *cis/trans* calculations.

Another indicator of the similarity between diazenes and their N-oxides concerns Engel's observation that mono-unsaturated five-membered rings are less strained than six-membered rings in the azo series, whereas the opposite obtains for hydrocarbons.¹⁴ In the monocyclic series, for example, the five-ring 16 was estimated to be 23.5 kJ mol^{-1} less strained than six-ring 10. The reverse is true by 18.4 kJ mol^{-1} for cyclohexene versus cyclopentene.¹⁶



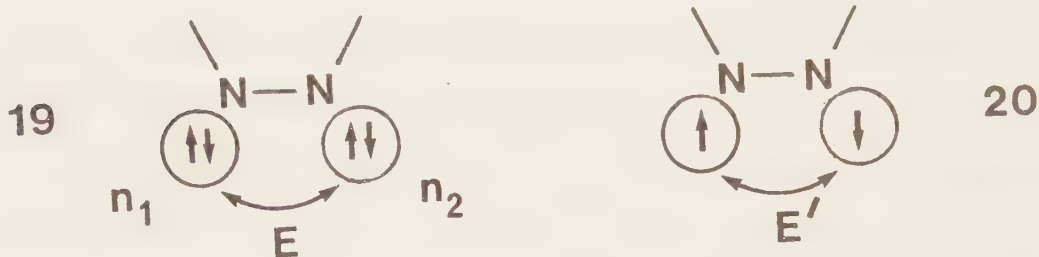
In the bicyclic series, the comparison is not so straightforward since the incorporation of the smaller ring in a bicycle seriously overwhelms other effects. Still, an evaluation of the qualitative trend is possible. Relative an Allen bond energy scheme, norbornene 17 is 50.2 kJ mol^{-1} more strained than bicyclooctene 18.³¹ The difference falls to 23.2 kJ mol^{-1} for azoalkanes 8 and 9. Thus, introduction of the N=N moiety into a five-membered ring of a simple hydrocarbon bicycle is $(50.2 - 23.2) = 27.0 \text{ kJ mol}^{-1}$ more favorable than substitution into a comparable six-ring. The same consideration for N-oxides 3 and 4 ($\Delta[S] = 14.9 \text{ kJ mol}^{-1}$) implies a gain of $(50.2 - 14.9) = 35.3 \text{ kJ mol}^{-1}$. As is the case for cyclic *cis* azo compounds, the azo N-oxides are strongly suggested to sustain a minimum of strain in the five-membered ring.

Finally, it is of interest to note that the bicyclo(2.2.2)-octene derivatives 4 and 9 are within experimental uncertainty strained to the same extent as the tetramethyl-monocycles 5 and 10, respectively (Table 5).

All in all, it appears safe to conclude that the strain characteristics of cyclic diazenes and diazene N-oxides are very similar both in terms of their response to structural variation and in the absolute magnitude of the strain energies. This, in turn, implies either that *lp-lp* repulsion in *cis* diazenes is not the determining factor in the *cis-trans* energy differential or that the *lp*/N-O repulsion is of the same order of magnitude. In order to gain insight into the situation, we have carried out additional PRDDO calculations on isomers 12-15 as described in the following segment.

A Model for Electron-Pair/Electron-Pair Repulsion

In principle the question of $lp-lp$ repulsion could be resolved by adopting a reliable procedure for calculating explicitly the repulsions between electron pairs located in molecular orbitals such as n_1 and n_2 in structure 19.



To a first approximation the *intra*-orbital repulsions can be neglected. However, the *inter*-orbital repulsions between electrons of both opposite and parallel spin would seem to be of importance. Were the interactions between all pairs of valence electrons in the molecule considered, an idea of the relative magnitude of the various pairwise interactions could be obtained providing the electrons exist essentially in discrete bonds and atom-centered nonbonded lone pairs. Within single-determinant Hartree-FOCK MO theory, the quantities of interest are the Coulomb (J_{mn}) and exchange (K_{mn}) repulsion integrals. The former represents the average repulsion of two electrons of opposite spin occupying orbitals ψ_m and ψ_n respectively.²³ The latter, K_{mn} , reflects the repulsion between two electrons of opposite spin in the same orbitals and is generally an order of magnitude smaller than J_{mn} .²⁴

Our model for electron-pair/electron-pair repulsion is thus constructed as follows. The PRDDO optimized geometries of the *cis*-

trans pairs 12-15 were subjected to a two-step molecular orbital localization in which the delocalized sigma and pi MO's were grouped together and localized separately according to the Boys' prescription.²⁵ In this way the heuristic view that a molecule can be viewed as a collection of nuclei superimposed with regional distributions of electron pairs (i.e., bonds and nonbonded pairs) is retained. Secondly, the Coulomb repulsion integrals for a selection of localized molecular orbital (LMO) pairs were calculated. The much less important exchange repulsion interactions between electrons of parallel spin have been ignored. For *cis* azomethane (12), for example, the $lp-lp$ repulsion energy (E in 19) is being modelled by the average repulsion between two electrons of opposite spin (E' in 20).

Summaries of the results for the set of LMO's considered in the present work are given in Figures 1 and 2. It will be evident that three types of sigma-sigma interactions have been evaluated: $lp-lp$, bond- lp and bond-bond.

Cis-Trans Energy Differences

Within the framework of the energy decomposition scheme outlined above, the origin of the *cis-trans* energy differences for diazenes and diazene N-oxides can now be addressed. The LMO-repulsion integral results for azomethane (Figure 1) permit several observations. First, as is usually the case for energy partitioning, the total energy differences ($\Delta E(trans - cis)$) are small and arise from the sums and differences of rather large numbers. Only a few of all possible electron repulsions are shown, but precisely those that

ought to change in response to isomerization from *trans* to *cis*. In addition, our analysis neglects nuclear repulsion, nuclear attraction and electron kinetic energy in keeping with the original intuitive hypothesis that the configurational azo energy spread is caused by nitrogen lone electron pair repulsion. Secondly, the *lp-lp*, bond-*lp* and bond-bond repulsions are all about the same order of magnitude. Thirdly, the interaction energies vary in an intuitively satisfying manner from the *trans* to the *cis* isomer. Thus, the C-N/C-N and *lp/lp* repulsions rise, while the C-N/*lp* quantities diminish. Fourth and most important, the largest contribution to the energy differences as far as electron repulsion is concerned centers around the C-H/C-H interactions on the methyl groups. Each alone is smaller than the others shown in the figure, but there are four of them and they are inflated on average by nearly 70%.

Specifically, as the more stable *trans* azomethane passes to the *cis* form, the C-N/C-N and *lp/lp* repulsion energies rise by 42 and 31 kJ mol⁻¹ respectively. Each C-H/C-H interaction, by strong contrast, is ballooned by some 210 kJ mol⁻¹ for a total increase of 840 kJ mol⁻¹. Thus the methyl-methyl repulsions are nearly thirty times more significant than the *lp-lp* interactions.

Within the limitations of the present model, the outcome is unambiguous. Classic steric effects provide the decisive contributions to isomer energetics. This is in complete accord with the observation that *cis* diazenes show greatly expanded CNN bond angles (12, 119.5°)²⁶ by comparison with the *trans* isomers²⁷ (13, 112.3 and 111.9°)²⁸ in spite of the postulated increase in *lp-lp* repulsion that is expected to accompany the angle deformation to larger values.^{14, 15}

Analysis of the azoxymethane *cis-trans* isomers 14 and 15 derives from the repulsion energies displayed in Figure 2. Again, several points are noteworthy. First, the calculated electron repulsions for the N-oxides are quantitatively very similar to those for the corresponding diazenes. Secondly, the $N^{\delta+}-O^{\delta-}$ /other electron-pair interactions are nearly identical for the two isomers and, in fact, involve the smallest energy difference from *trans* to *cis* (-13 kJ mol^{-1}). Thirdly, as for the azo species, isomerization to the *cis* form causes a modest increase in the energy of the C-N/C-N (34 kJ mol^{-1}), N-O/ N_{lp} (42 kJ mol^{-1}) and O_{lp}/N_{lp} (139 kJ mol^{-1}) interactions. Finally, the change in the C-H/C-H repulsions dominates ($4 \times 200 \text{ kJ mol}^{-1}$). The latter are six times more important than the next largest contribution, namely the $1,3-N_{lp}/O_{lp}$ interactions. Interestingly, while the partitioned energy increase for methyl group crowding is very similar for the azo and azo N-oxide isomer couples, the $1,3-N_{lp}/O_{lp}$ enhancement is calculated to be nearly five times the magnitude of the $1,2-N_{lp}/N_{lp}$ quantity.

The assignment of the methyl steric repulsion effect as responsible for the greater stability of the *trans* N-oxide isomer is likewise in agreement with angle deformation about CNNC upon isomerization. Relative to *trans* azomethane, the NNC angle expands by $5-7^\circ$ (i.e., to $117.6-119.1^\circ$)²⁹ similar to that for *cis* azomethane. The NN(O)C angle breathes to the extent of $12-14^\circ$ (i.e., to $122.0-126.2^\circ$)²⁹ probably in part in response to the rehybridization from di- to trivalent nitrogen.³⁰

The ability of the N-oxides to sustain greater angle deformation in the *cis* isomer relative to the diazenes raises the question as to

why the calculated isomerization energies for the former are greater than the latter (42/72 versus 28/54 kJ mol⁻¹, respectively; PRDD0/4-31G). The angle opening ought to stabilize preferentially the *cis* azoxy moiety. One possibility is the operation of this influence simultaneous with an even greater stabilization of the *trans* N-oxide by comparison. Brunck and Weinhold⁸ have suggested a mechanism whereby the *trans* disposition of the nitrogen lone pair to the N-O bond (15) might well be more stabilizing than the corresponding *cis* (14) relationship. That is, the *trans* bond-antibond interaction is strong and more energy lowering than is the *cis* interaction.

Conclusion

It would appear that the experimental ($\Delta H_f^0(g)$) and the theoretical considerations converge to permit the interpretation that *lp-lp* repulsions in dialkyl diazenes are not responsible for the thermochemical energy differences between configurational isomers. Electron-pair repulsions modelled by two electron Coulomb repulsion integrals are of near equal importance for *lp-lp*, *lp-bond* and *bond-bond* interactions. The exception lies in the C-H/C-H repulsions, the sum of which is calculated to dominate the energy comparisons. From a classical point of view, both diazene and diazene N-oxide *cis-trans* energy differences are adequately described by steric repulsion effects between alkyl substituents. Not surprisingly, this principle has been successfully adopted in two separate force-field parameterizations for azoalkanes.^{19, 20}

Acknowledgements

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Experimental Section

Quantum Mechanical Calculations

For *cis* and *trans* azomethane, the PRDDO calculations²¹ were carried out on the experimental electron diffraction geometries of Stevens et al.²⁶ and Almenningen et al.²⁸ respectively; i.e., on conformations 12 and 13. These same structures were employed for the Boys LMO and subsequent repulsion integral treatment. At the 4-31G level²² a full optimization of all internal variables for conformers 12 and 13 with assumed C-N=N-C planarity was performed (cf. Table 6). Several conformations of the isomers of azoxymethane were preliminarily optimized with the semi-empirical MNDO method.³² The lowest energy forms, 14 and 15, were then reoptimized with both PRDDO and the 4-31G basis; heavy atom planarity was assumed.

Compounds

The N-oxides 3-6 are stable at their melting points. Their purity was checked by the stepwise scanning method of d.s.c.³³ For N-oxide 7, which decomposes slowly at its melting point, a continuous scan melting curve was obtained by d.s.c. with a scan rate of 2.5 K min⁻¹. Plots of the equilibrium temperature versus the reciprocal of the fraction melted showed a curvature for all compounds except 5. The dynamic method is not capable of discriminating whether the curvature is due to lack of equilibrium or to factors such as the formation of solid solutions. With the stepwise method, however, this can be done. The curvature for compounds 3, 4 and 6 was therefore ascribed to the existence of solutions in the solid phase. This was taken into account in the analysis of the results. The purity of all five compounds was shown to be >99.9 mole-%.

G.l.c. could not be used as an additional purity check, since at temperatures where the N-oxides are stable their vapor pressures are too low. As a complement to the d.s.c. measurements an h.p.l.c. purity determination was made. Good agreement was obtained in all cases.

The samples were dried by sublimation through molecular sieves. Water content was determined by a gas chromatographic technique.³⁴ All five N-oxides contained some water for which a correction has been applied (see Table 7).

Combustion Calorimetry - Apparatus and Procedure

The rotating bomb calorimeter TKL-3 was used with platinum-lined bombs 3C (3, 6) and 3B (4, 5 7)³⁵ with internal volumes of 0.2620 and 0.2609 dm³, respectively. Calibration experiments were performed by burning benzoic acid, National Bureau of Standards SRM 39i, under certificate conditions. The temperature was measured by means of a Hewlett Packard Quartz Thermometer in its 100 s mode (resolution 10⁻⁵ K).

The samples were burned as pellets enclosed in polyester (Mylar) bags. Paraffin oil, designation TKL-66A,³⁶ was used as a combustion aid. The specific standard energies of combustion for the Mylar and the paraffin oil were $-(22896.9 - 1.056 \cdot RH \pm 3.3) \text{ J g}^{-1}$ (RH = relative humidity) and $-(46044.3 \pm 2.0) \text{ J g}^{-1}$, respectively. Details of the calorimetric procedure have been previously described.³⁷ All combustions were carried out with an initial pressure of oxygen of 3.04 MPa at 298.15 K. At least six combustions were carried out for

each N-oxide. The initial volume of water was 3.0 cm^3 (3, 6) and 10.0 cm^3 (4, 5, 7) respectively. The ignition energy was measured in each experiment. In all experiments except two, the compounds burned well without any traces of soot deposit.

All weighings were reduced to masses; molar masses were computed from the 1977 table of atomic weights.³⁸ The corrected temperature rise, $\Delta\theta$, and the energy equivalent of the system, $\epsilon^0(\text{calor})$, were calculated as described by Bjellerup.³⁹

Combustion Calorimetry - Analytical Procedure

After each experiment the bomb gases were passed through a tube for CO-analysis (Dräger). This test has a detection limit of less than 10^{-6} mole fraction of CO. The total amounts of HNO_2 and HNO_3 in the final bomb solutions were determined by titration with 0.02-molar carbonate-free NaOH. Endpoints were determined such that carbonic acid was not titrated. The HNO_2 concentration was measured colorimetrically by means of the Griess method.⁴⁰ The concentration of HNO_2 was low, between 0.2-1.0% of that found for HNO_3 . The lower values occurred for combustions with the smallest initial volume of water.

Vaporization Calorimetry

The enthalpies of sublimation for the five N-oxides were measured with the Morawetz type calorimeter,⁴¹ the compounds being sublimed into the calorimeter. Since the pressure-volume work is reduced in these measurements, it is necessary to apply a correction in order

to obtain the enthalpy of sublimation. The corrections amounted to 0.92 kJ mol^{-1} for N-oxide 3 and 1.72 kJ mol^{-1} for the other N-oxides.

N-oxide 3 has a solid state transition at 303.4 K. Its enthalpy of transition ΔH_{trs} was measured by d.s.c. The average value from four separate runs was $(8.12 \pm 0.08) \text{ kJ mol}^{-1}$. It was observed from the d.s.c. measurements that the high-temperature phase could be undercooled by approximately 20 K. The vaporization calorimeter was therefore cooled to 278 K to ensure that compound 3 was in its thermodynamically stable form at 298.15 K. As an extra check, the calorimeter was heated above the transition temperature and two experiments were performed on the undercooled high-temperature phase. The results from these experiments were $(68.3 \pm 1.5) \text{ kJ mol}^{-1}$. This value combined with the enthalpy of transition provides an enthalpy of sublimation of the low-temperature phase of $(76.4 \pm 1.5) \text{ kJ mol}^{-1}$ in perfect agreement with the value listed in Table 3.

Calculation of Calorimetric Results

For the calculations of the corrections to standard states, ΔU_{Σ} , a computer program based on the procedure in Ref. 42 was used. The energy of solution of carbon dioxide $\Delta U_{\text{soln}}(\text{CO}_2)$ was taken as $17.09 \text{ kJ mol}^{-1}$ ⁴³ and the solubility constant $K(\text{CO}_2)$ as $0.3395 \text{ mol dm}^{-3} \text{ MPa}^{-1}$ ⁴³ both at 298.15 K. The energy of decomposition of nitric acid $\Delta U_{\text{dec}}(\text{HNO}_3)$ and of nitrous acid $\Delta U_{\text{dec}}(\text{HNO}_2)$ were taken as 58.89 and $-27.6 \text{ kJ mol}^{-1}$, ⁴² respectively. Some auxiliary quantities used in the calculations are given below. The N-oxide densities employed are 1.20 (3), 1.19 (4, 6), 1.04 (5), and 1.21 (7) g cm^{-3} .

Estimates of $(\partial v/\partial T)_p = 0.7 \text{ mm}^3 \text{K}^{-1} \text{g}^{-1}$ and $c_p = 1.5 \text{ J K}^{-1} \text{g}^{-1}$ were used for all five compounds. The final overall precision of the Δu_C^0 mean value was calculated as outlined previously.⁴⁴ Here the quantity q_5 stands for the energy of decomposition of nitric and nitrous acid. The ratio s_5/q_5 was taken as 0.01.

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TABLE 1. Summary of typical combustion experiments.

$$\Delta u_C^O(\text{oil}) = -(46044.3 \pm 2.0) \text{ J g}^{-1}; \quad \Delta u_C^O(\text{Mylar}) = -(22896.9 - 1.056 \cdot RH \pm 3.3) \text{ J g}^{-1};$$

The standard deviation of the mean for the two calibration series were 0.9 J K^{-1} (3, 6) and 0.6 J K^{-1} (4, 5 and 7) respectively.

	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
m(comp)/ g	0.422301	0.463929	0.304521	0.423366	0.383796
m(oil) /g	0.175717	0.144014	0.186528	0.168989	0.177302
m(Mylar)/ g	0.048643	0.040310	0.041004	0.038395	0.047425
m(fuse) /g	0.001070	0.001240	0.001356	0.001410	0.001200
m(pt)/ g	11.272	9.193	9.193	11.272	9.193
Δ^A/K	0.740752	0.755254	0.697625	0.739189	0.745310
$\epsilon^O(\text{calor})/ \text{ J K}^{-1}$	28674.0	28672.8	28672.5	28673.8	28672.7
$m^i(\text{cont})/ \text{ g}$	25.21	29.80	29.69	25.19	29.76
$\epsilon^i(\text{cont})/ \text{ J K}^{-1}$	22.70	51.29	51.15	22.68	51.25
$\Delta U_{\text{soln}}(\text{CO}_2)/ \text{ J}^a$	5.64	17.42	15.75	5.68	17.41
$\Delta U_{\text{dec}}(\text{HNO}_3 + \text{HNO}_2) / \text{ J}$	42.30	41.56	33.99	40.18	41.24
$\Delta U_{\Sigma} / \text{ J}$	12.30	23.15	19.56	12.74	23.08
$-\Delta u_C^O(\text{comp})/ \text{ J g}^{-1}$	28188.4	30029.2	33984.4	29285.2	31220.56

a) This term is included in ΔU_{Σ} .

TABLE 2. Results of combustion experiments at 298.15 K.

	$-\Delta u_c^0/\text{kJ g}^{-1}$						
	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>		
	28.1647	30.0370 ^b	33.9844	29.2755	31.2284		
	28.1987	30.0486	33.9780	29.2753	31.2206		
	28.1835	30.0402	33.9732	29.2852	31.2044		
	28.1808	30.0255	33.9593	29.3127	31.2163		
	28.1884	30.0161	33.9564	29.3073	31.2063		
	28.1843	30.0331	33.9693	29.2876	31.2157		
			33.9926		31.2051		
Mean:	28.1834		33.9733	29.2906	31.2138		
Corrected mean: ^a	28.1871	30.0331	33.9893	29.2956	31.2226		
Standard deviation of the corrected mean:	0.0046	0.0046	0.0051	0.0066	0.0036		

a) Corrections applied for water content. See Table 7.

b) Corrections applied in the individual results. See Table 7.

TABLE 3. Results from sublimation experiments at 298.15 K.

Compound	Number of Experiments	$(\Delta H_{\text{sub}}^0 \pm 2 \text{ s}) \text{ kJ mol}^{-1}$
<u>3</u>	6	76.82 $\pm$ 0.51
<u>4</u>	5	91.25 $\pm$ 0.98
<u>5</u>	6	91.93 $\pm$ 0.78
<u>6</u>	4	87.29 $\pm$ 1.00
<u>7</u>	6	93.38 $\pm$ 1.16

TABLE 4. Results and derived quantities at 298.15 K. The uncertainties given are twice the final overall standard deviations of the means.^a

Compound	$-\Delta U_C^0/\text{kJ mol}^{-1}$	$-\Delta H_C^0/\text{kJ mol}^{-1}$	$\Delta H_f^0(\text{s})/\text{kJ mol}^{-1}$	$\Delta H_f^0(\text{g})/\text{kJ mol}^{-1}$
<u>3</u>	3160.7 ± 1.1	3161.9 ± 1.1	51.0 ± 1.3	127.8 ± 1.4
<u>4</u>	3788.9 ± 1.3	3791.4 ± 1.3	1.2 ± 1.6	92.4 ± 1.9
<u>5</u>	5310.1 ± 1.8	5316.3 ± 1.8	-118.5 ± 2.1	-26.5 ± 2.2
<u>6</u>	3636.8 ± 1.7	3638.1 ± 1.7	133.7 ± 1.9	221.0 ± 2.1
<u>7</u>	4314.0 ± 1.2	4316.5 ± 1.2	132.8 ± 1.5	226.1 ± 1.9

a) Values for the enthalpies of formation for gaseous carbon dioxide and liquid water used in the calculations were taken from Ref. 45.

TABLE 5. Apparent strain energies for the diazene N-oxides and some corresponding diazenes.^a

diazene N-oxide	[S] kJ/mol ⁻¹	diazene	[S] kJ/mol ⁻¹
<u>3</u>	61.5 $\pm$ 1.4	<u>8</u>	59.3 $\pm$ 2.7
<u>4</u>	46.6 $\pm$ 1.9	<u>9</u>	36.1 $\pm$ 4.4
<u>5</u>	44.9 $\pm$ 2.1	<u>10</u>	31.6 $\pm$ 4.5
<u>6</u>	61.6 $\pm$ 2.1		
<u>7</u>	171.9 $\pm$ 1.9		

a) The uncertainties given are twice the overall standard deviation of the mean of the experimental enthalpies of formation.

TABLE 6. Molecular geometries and energies for cis and trans azoxymethane conformations 14 and 15 as determined by PRDDO and 4-31G optimizations.

structural parameter, θ , deg.	PRDDO		4-31G	
	<u>cis</u>	<u>trans</u>	<u>cis</u>	<u>trans</u>
rN=N	1.322	1.315	1.233	1.229
rN-O	1.289	1.286	1.233	1.292
rC-N	1.459	1.462	1.456	1.452
rC-N(O)	1.500	1.504	1.477	1.460
$\angle$ NNO	122.2	126.6	122.0	125.5
$\angle$ NNC	117.8	111.5	119.5	115.6
$\angle$ NN(O)C	123.1	115.2	123.8	118.5
$\angle$ CNO	114.7	118.3	114.2	116.0
E /au	-262.16431	-262.18018	-262.438058	-262.465322

TABLE 7. Corrections for water content.

Compound	Water content/mass per cent	Correction/Jg ⁻¹
<u>3</u>	0.013 $\pm$ 0.004	3.7 $\pm$ 1.1
<u>4</u>	0.028 $\pm$ 0.004 ^a	8.3 $\pm$ 1.2
<u>5</u>	0.047 $\pm$ 0.004	16.0 $\pm$ 1.4
<u>6</u>	0.017 $\pm$ 0.004	5.0 $\pm$ 1.2
<u>7</u>	0.028 $\pm$ 0.004	8.7 $\pm$ 1.2

a) A correction for 0.026 mass per cent was applied in four experiments, and for 0.031 mass per cent i two experiments

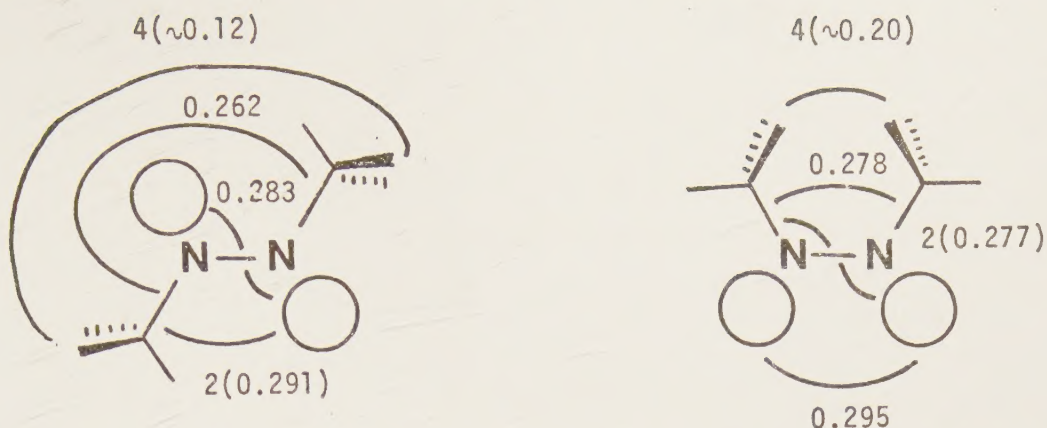


FIGURE 1. Two electron Coulomb repulsion energies (au) over the pair of Boys' localized molecular orbital (LMO) pairs indicated for cis and trans azomethane conformers 12 and 13.

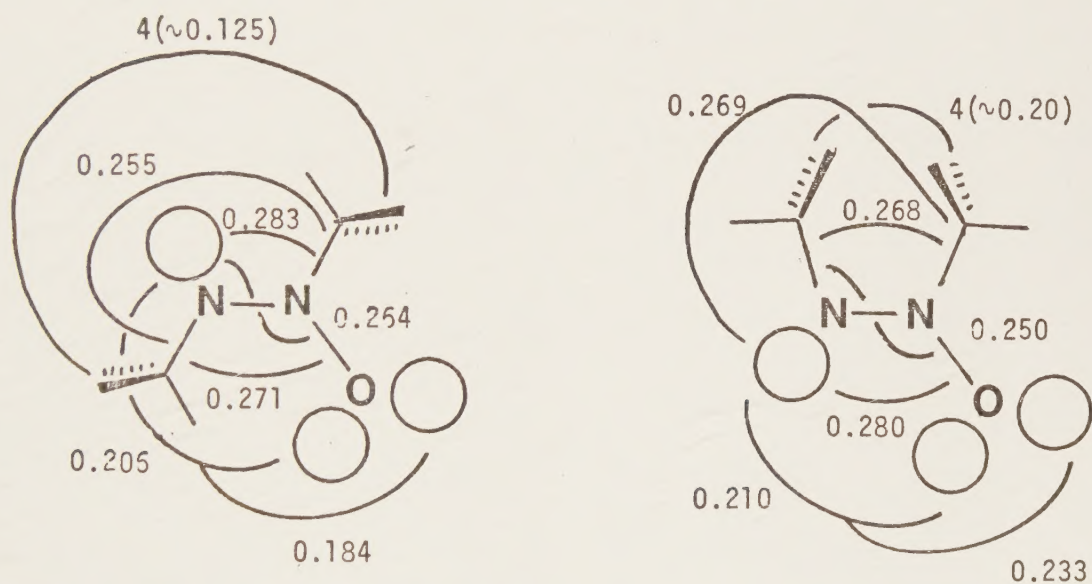


FIGURE 2. Two electron Coulomb repulsion energies (au) over the pair of Boys' localized molecular orbital (LMO) pairs indicated for cis and trans azoxymethane conformers 14 and 15.

